VANADIUM DIOXIDE NANOCOMPOSITE COATINGS AS FENESTRATION ELEMENTS

An Undergraduate Research Scholars Thesis

by

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ABSTRACT

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Smart windows have attracted interest as a method of reducing the energy consumption of buildings. These smart windows would be able to reflect and transmit infrared (IR) light in response to ambient temperature, while also retaining the ability to transmit daylight. Vanadium dioxide is a prime candidate for use in smart windows due to the fact that its transition temperature of 67˚C is far closer to room temperature than is typical of materials exhibiting a reversible metal—insulator transition; the transition temperature can be further depressed by introducing dopants. Above this transition temperature, vanadium dioxide switches from an insulator to metal and is able to reflect IR light. This characteristic would efficiently cut down energy consumption, as the smart windows would be able to regulate temperatures inside of buildings with reduced aid of air-conditioning systems. Vanadium dioxide alone produces a very poor film and therefore must be interfaced with a different material for practical application. Previously, our group found that silica matrices could be utilized to form films with VO_2 via a modified Stöber method. These films were formed utilizing spray coating, and though somewhat successful, the method did not provide scalable or consistent films. Later, VO_2 was dispersed in thickening agents to further stabilize dispersions and casting was performed with a casting knife,

which improved film consistency. In this work we are focusing on functionalizing the surface of VO_2 or $VO_2@SiO_2$ nanocrystals in solution with a perfluorinated silane that will work in tandem with fluorinated surfactants to disperse these materials within acrylic acid matrices. Surface functionalization of the VO_2 will protect the material from oxidation as well as allowing the use of a surfactant to reduce agglomeration, which has been found to be a problem in previous work, thereby yielding a more homogeneous distribution of particles within films. Optimization of the Stöber method by changing experimental parameters related to the shell precursor and catalyst were investigated to reduce the overall agglomeration of VO_2 nanoparticles in the silica shell.

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CHAPTER I

INTRODUCTION

Energy consumption has increased worldwide and is projected to reach 40 TW by 2050; meeting the energy needs of a growing population has emerged as an urgent imperative.[1] A solution that has come into play is the emergence of "smart" windows. Dynamically switchable "smart" windows that enable modulation of solar heat gain depending on the outside temperature are of great interest for reducing the energy footprint of residential and commercial buildings. In our proposed "smart" window constructs, infrared transmittance is greatly modulated as the result of a structural and electronic phase transition in the binary vanadium oxide VO_2.[2] This material switches reversibly from an infrared transmitting insulating phase at low temperatures to an infrared reflective metallic phase at high temperatures.[3] The transition temperature is tunable by size and incorporation of dopant atoms within the nanowires.[4]

Past work demonstrated by this research group has focused on the synthesis of nanostructured VO_2.[4] However, such powders alone do not yield a suitable film and therefore must be interfaced with a different material for practical applications. Previously, our group found that silica matrices could be utilized to form films with vanadium dioxide *via* a modified Stöber method.[2] These films were formed *via* spray coating, and although some success was achieved, the method did not provide scalable or consistent films. More consistent films were produced through a casting method in which films were deposited as viscous dispersions of VO_2 within an acrylic polymeric additive, methacrylic acid/ethyl acrylate. Although these films provided better results, problems arose with agglomeration of the nanoparticles as well as the

dispersion of the VO_2 in solution. In this work, it was hypothesized that optimizing the Stöber method would reduce shell thickness of the silica shell and in return reduce agglomeration of VO_2 nanoparticles. A second solution involves functionalizing the surface of VO_2 or $VO_2@SiO_2$ nanocrystals in solution with a perfluorinated silane that will work in tandem with fluorinated surfactants to disperse these materials within acrylic acid matrices. Overall, we predict that by reducing agglomeration and improving the dispersion of nanoparticles in solution, a more consistent film with better optical results can be produced.

CHAPTER II

EXPERIMENTAL

Preparation of Silica Shells around VO_2 Nanocrystals

VO_2 nanocrystals were synthesized through an aqueous-phase route. This procedure was created by designing a two-step procedure by modifying previously reported works.[5,6] The first step involves the synthesis of $VO(OH)_2$ as a precipitate from a reaction between ammonium metavanadate and hydrazine in deionized water at 80°C. In the second step of this procedure hydrothermal annealing of the $VO(OH)_2$ precipitate in a hydrothermal vessel at 210°C for 24—72 h was performed. The solution was placed into a centrifuge tube and centrifuged at 8,500 rpm for 10 min. The supernatant was then decanted and the remaining sample was suspended in acetone via ultrasonication. The sample was centrifuged at 8500 rpm and the supernatant was decanted. This process was repeated for three washes and the sample was collected the next day after it was allowed to air dry.

Silica shells and films were grown through a modified Stöber method that has been developed in this group's past work.[7] In a typical reaction, a combination of hydrolysis and condensation reactions are used to constitute a SiO_2 shell around the VO_2 nanoparticles. A 4:1, ethanol: water, ratio was used where 32 mL of ethanol and 8 mL of nanopure water were placed in a round bottom flask with ~24 mg of ultrasmall VO_2. This mixture was then ultrasonicated for ~10 minutes in order to disperse the VO_2. Varying amounts of NH_4OH, from 200—500 μL, were added drop wise to the solution while subjecting the reaction mixture to continuous ultrasonication. Varying amounts of tetraethyl orthosilicate (TEOS), from 50-200 μL, were also

added to the dispersion and the sample was allowed to sonicate for 25 min. Improvements have been seen in ultrasmall coatings when the reaction time was reduced from 25 to 20 min. The ultrasonicated dispersion was centrifuged to collect the sample. The solution was placed into a centrifuge tube and centrifuged at 8,700 rpm for 10 min. The supernatant was then decanted and the remaining sample was washed with ethanol and centrifuged an additional time at 8,700 rpm for 10 min. This process was repeated for 3 washes and the sample was collected the next day after it was allowed to air dry.

In order to optimize the thickness of the SiO_2 shell, the amount of the catalyst and the silane precursor were varied as well as reaction time. The reaction timed varied between 15 min, 20 min, and 25 min. All other parameters were kept constant. TEOS was used in a range from 50-200 μL and NH_4OH was used in range of 200-500 μL for every 24 mg of VO_2.

Surface Functionalization of Silica-Coated Vanadium Dioxide

The VO_2@SiO_2 nanowires were functionalized prior to their addition to a methacrylic acid/ethyl acrylate solution. 24 mg of VO_2 was placed in 2.0 M trimethoxy(1H,1H,2H,2H-perfluorooctyl)silane solution in a plastic vial. This solution consisted of 135 μL of trimethoxy(1H,1H,2H,2H-perfluorooctyl)silane and 20 mL of tetradecafluorohexane. The solution was sealed with parafilm and allowed to stir overnight using a magnetic stirrer. The next day, the solution was placed into a centrifuge tube and centrifuged at 8,700 rpm for 10 min. The supernatant was then decanted and the remaining sample was washed with tetradecafluorohexane and centrifuged once again at 8,700 rpm for 10 min. This process occurred for a total of three washes and the sample was collected the next day after being allowed to air dry.

Once the sample was allowed to dry, varying amounts of the VO_2 nanoparticles, from 2-16 mg, were added to a series of vials. Varying amounts of PFOS surfactant, depending on the desired amount of VO_2, were also added to the vial and the solution was sonicated to disperse the VO_2 in water. Once the nanoparticles were well dispersed 330 μL of methacrylic acid/ethyl acrylate were added to the solution and the methacrylic acid/ethyl acrylate procedure was continued to create a viscous solution for film application.

Film Casting with Methacrylic Acid/Ethyl Acrylate

The solution was thickened for film application with the addition of methacrylic acid/ethyl acrylate. The viscous solution was produced by adding 9.67 mL of nanopure water, at a pH ranging from 11.5—11.6, to a vial containing the desired amount of VO_2 and PFOS as stated previously. The solution was sonicated for 10 min to disperse the VO_2 in the solution. The solution was placed on a magnetic stir plate and 330 μL of methacrylic acid/ethyl acrylate was added to the stirring solution. The mixture was vigorously stirred and allowed to stir for 20 min until all of the methacrylic acid/ethyl acrylate was dispersed in the solution. A glass slide cleaned with ethanol was placed on a flat platform and 2 mL of the VO_2 methacrylic acid/ethyl acrylate solution was deposited tracing a line down the middle of the slide. A film-casting knife at a set height of 1 mm was used to drag the solution from the top of the slide to the bottom in a uniform matter. The coated glass slide was then allowed to dry overnight.

Instrumentation

A multi-wavelength Bruker Vertex-70 FTIR spectrometer equipped with a Pike Technologies variable temperature stage was used to characterize the films across the UV-Vis-NIR range of the electromagnetic spectrum.

The VO_2@SiO_2-F nanoparticles interfaces were examined using high-resolution transmission electron microscopy (HRTEM) (JEOL-2010, operated with an accelerating voltage of 200 kV and a beam current of 100 mA). The samples for HRTEM were prepared by dispersing the VO_2@SiO_2-F nanoparticles in ethanol and placing the solution on a 300-mesh copper grid coated with amorphous carbon. The grid was then allowed to dry under ambient conditions. HRTEM was performed using a JEOL JEM-2010 instrument operated at 200 kV acceleration voltage.

CHAPTER III

RESULTS & DISCUSSION

Optimization of the Stöber Method for VO_2 Nanoparticles

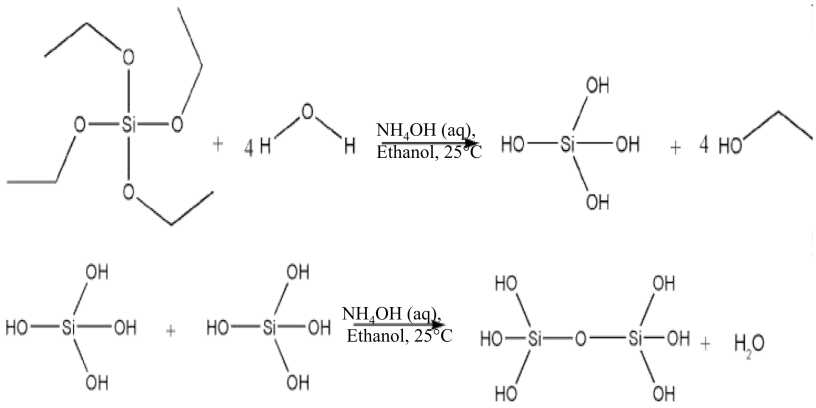


Figure 1. Unmodified Stöber reaction comprising a hydrolysis and condensation reaction.

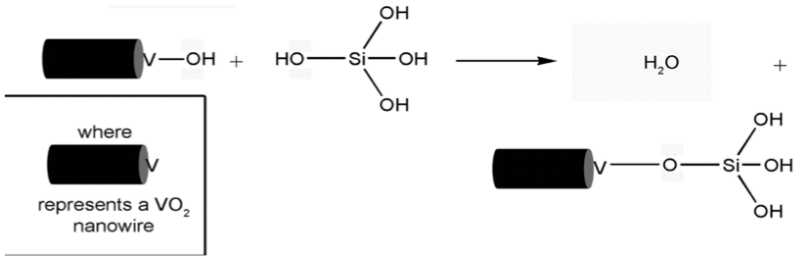


Figure 2. Modification of the Stöber method wherein VO_2 nanowires are added during the condensation part of the reaction.

In previous work, VO_2 nanowires have been interfaced in silica matrices through a modified Stöber as seen in figures 1 and 2. TEOS undergoes a hydrolysis reaction to produce orthosilicic acid. The product of this reaction is then condensed to produce the silica matrix encapsulating the VO_2 nanowires.

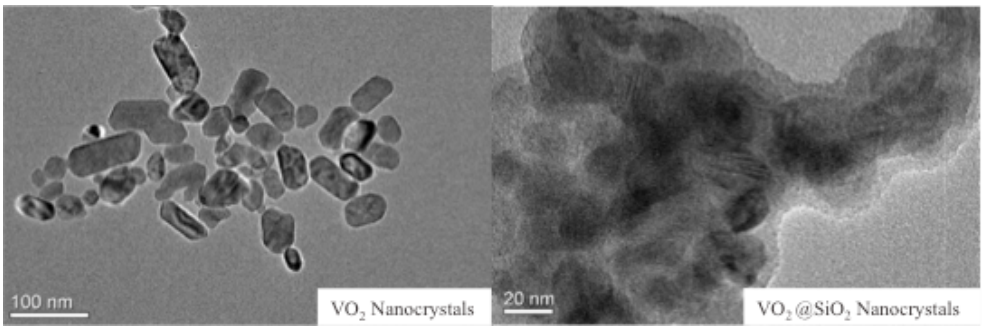


Figure 3. TEM images of bare VO_2 nanocrystals on the left and silica coated VO_2 nanocrystals via Stöber method on the right.

Although this method has been proven to successfully produce a silica shell around VO_2, the $VO_2@SiO_2$ still displays agglomeration of the nanoparticles within the matrix. From the TEM images in figure 3 it can be seen that clusters of VO_2 nanoparticles are residing within the shells instead of being individually encapsulated. This agglomeration of nanoparticles greatly reduces NIR modulation as well as transmission in the visible spectrum.

To reduce agglomeration, the Stöber method was optimized to individually coat the nanoparticles while reducing the thickness of the silica shell. The parameters that were changed in the Stöber reaction include the amounts of shell precursor TEOS, and the catalyst, NH_4OH. In figure 4, the success of the varying parameters can be seen. From all the samples produced, the most promising trial was the sample produced with 50 μL of TEOS and 400 μL of NH_4OH.

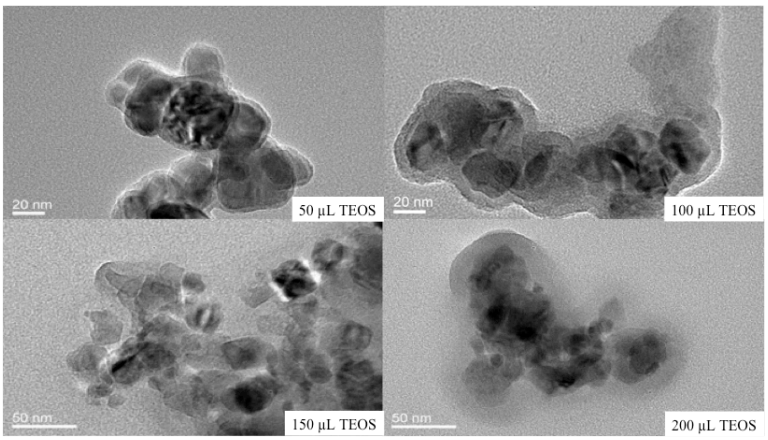


Figure 4. TEM images of silica-coated ultrasmall VO_2 nanoparticles via optimized Stöber method consisting of 400 µL of NH_4OH and varying amounts of TEOS.

Through TEM imaging of all trials, it was shown that the change in the amount of NH_4OH had minimal impact on the shell thickness while maintaining the amount of TEOS constant. As a result, TEOS was found to be the parameter that controls shell thickness. In the TEM images featured in figure 4, an increase of TEOS evidently increases the shell thickness. This conclusion can clearly be seen when comparing the 50 µL TEOS sample to the sample prepared with 200 µL of TEOS, as only a thin shell can be observed surrounding the nanoparticles. In conjunction with this discovery it can be seen that agglomeration is reduced. In the 150 µL TEOS sample in figure 4, clusters are still forming within the silica shell but a lot less than previous samples.

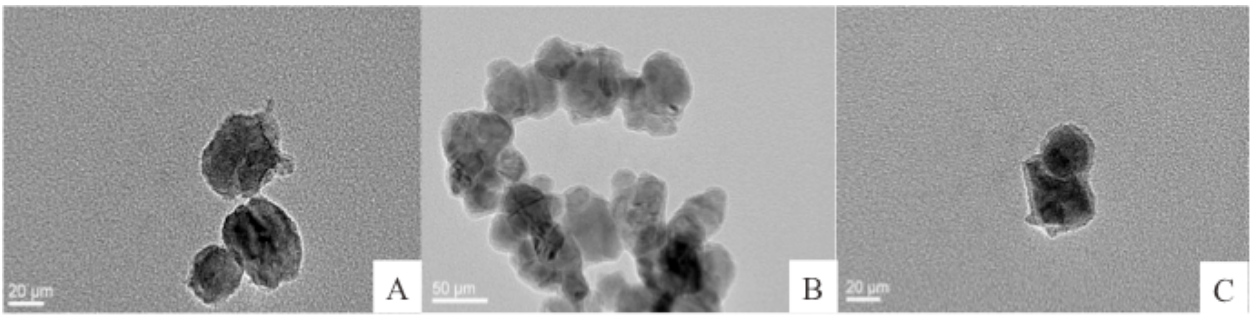


Figure 5. TEM images of silica coated ultrasmall VO_2 nanoparticles *via* optimized Stöber method consisting of 400 µL of NH_4OH, 50 µL of TEOS, and varying reaction times. Image A pictured on the top is at a reaction time of 15 min and images B and C were allotted a reaction time of 20 min.

To further optimize the Stöber method, reaction times were also varied while maintaining a constant use of 50 µL of TEOS, and 400 µL of NH_4OH. By varying reaction times, it was possible to determine if cutting down sonication time would create a thinner shell or result in an incomplete reaction. Evidence in figure 5 shows that reducing reaction time also reduces shell thickness. The TEM image A, in figure 5, depicts a nanoparticle that was coated for a reaction time of 15 min and as a consequence the reaction did not reach completion. Images B and C were allotted a reaction time of 20 min and a thinner shell was produced when compared to the constant of 25 min.

Surface Functionalization of Vanadium Dioxide

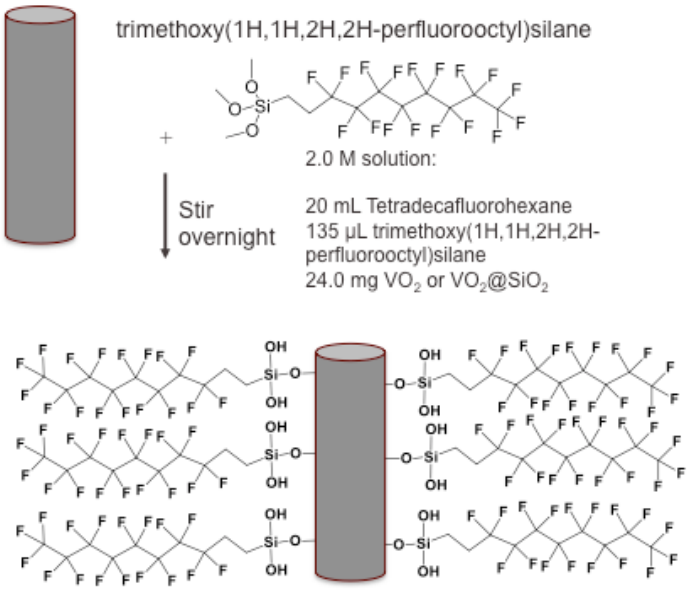


Figure 6. Reaction scheme for the surface functionalization of VO_2 nanowires.

Although optimization of the Stöber method provided very promising results, surface functionalization of VO_2 in theory had some propitious qualities as well. Surface functionalization of VO_2 nanoparticles follows the same reaction scheme as the Stöber method but with some slight changes. Instead of TEOS, trimethoxy(1H,1H,2H,2H-perfluorooctyl) silane, was used as seen in figure 6. The major differences between these two reagents is the presence of methoxy groups as opposed to ethoxy groups and a fluorinated chain is in place of an additional ethoxy group in TEOS. Siloxane functionalization allows for grafting of a wide range of functional groups, such as fluorinated and other hydrophobic chains.

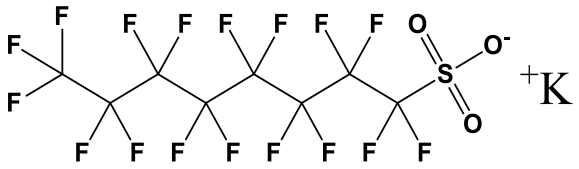


Figure 7. Fluorinating surfactant, potassium perfluorooctanesulfonate (PFOS).

PFOS, pictured in figure 7, in this reaction acts as the fluorinated surfactant. This surfactant provides the VO_2 nanoparticles with a slight negative surface charge, as the perfluorinated groups on PFOS are attracted to the perfluorinated groups on the already silanized nanoparticles. The negatively charged $R\text{-}SO_3^-$ functional groups bring about dispersibility of the nanoparticles in water and polar media through ion-dipole interactions thus causing a decrease in agglomeration. The PFOS surfactant also allows for the fluorinated VO_2 nanoparticles to be dispersed in aqueous environments as seen in figure 8. This in turn also facilitates the casting of well-dispersed, uniform films.

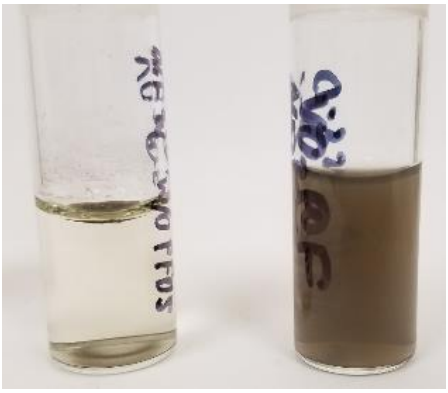


Figure 8. Images of fluorinated VO_2 before the addition of the PFOS surfactant, on the left, and after, pictured on the right.

Film Application of Functionalized Vanadium Dioxide

Concentration of Sample	Max NIR drop (%)	Max Vis (%)
VO_2@SiO_2 2 mg/10 mL	**6**	**89**
VO_2 2 mg/10 mL	**12.4**	**74.8**
VO_2@SiO_2 4 mg/10 mL	**12**	**80**
VO_2 4 mg/10 mL	**20**	**60**
VO_2@SiO_2 6 mg/10 mL	**15**	**71**
VO_2 6mg/10mL	**22**	**47**
VO_2@SiO_2 8 mg/10 mL	**22**	**54**
VO_2 8mg/10 mL	**22**	**44**
VO_2@SiO_2 10 mg/10 mL	**22**	**42**
VO_2 10 mg/10 mL	**22**	**38**

Figure 9. Previously recorded Optical IR data for non-functionalized VO_2/VO_2@SiO_2. All samples were placed in a 10 mL solution of methacrylic acid/ethyl acrylate.

In previous work non-functionalized VO_2 produced poor results as seen in figure 9. As the concentration of the VO_2 was increased the drop in the NIR also increased but transmittance in the visible range dropped dramatically. The highest drop in the NIR was 22% while giving poor visibility. Therefore functionalization of the VO_2 was brought up as a solution to provide better dispersion of VO_2 in solution to produce more optimal films.

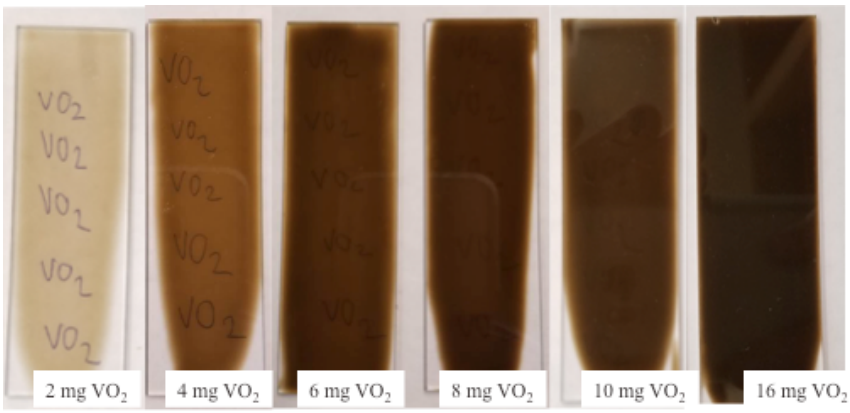


Figure 10. From left to right: Films cast from 10 mL solutions of methacrylic acid/ethyl acrylate containing 2, 4, 6, 8, 10, and 16 mg fluorinated VO_2. Films coated *via* casting knife.

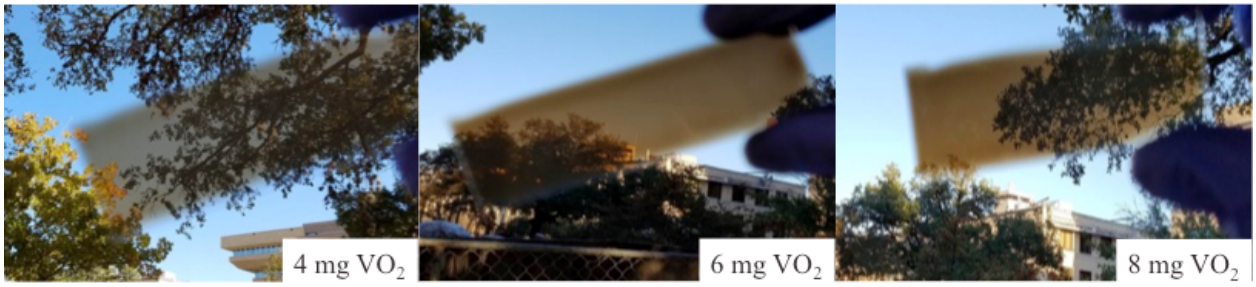
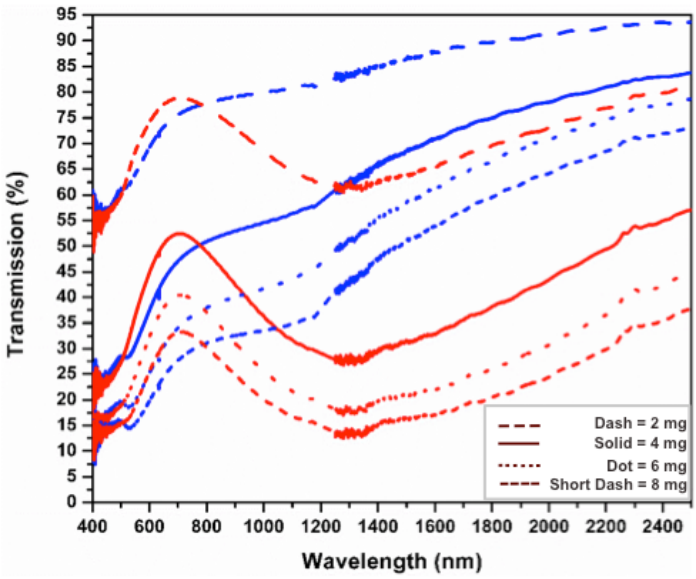


Figure 11. From left to right: films cast from 10 mL solutions of methacrylic acid/ethyl acrylate containing 4, 6, and 8 mg fluorinated VO_2. Films coated via casting knife and exposed to natural light.

To determine the degree of success in reducing agglomeration by use of functionalized VO_2, films were created. First fluorinated VO_2 was tested and casting of these films produced uniform films overall as seen in figures 10 and 11. Dispersion of the VO_2 particles was increased with the use of the fluorinating surfactant. These films were created with only varying amounts of VO_2 to determine how much VO_2 is required to produce higher degrees of modulation while maintaining high visible light transmission. Uncoated VO_2 was fluorinated to determine how well surface functionalization does without the use of a silica shell.



	NIR drop (%)	Max Vis (%)
2 mg/10 mL	**23.3**	**78.9**
4 mg/10 mL	**38.2**	**52.4**
6 mg/10 mL	**41.0**	**40.4**
8 mg/10 mL	**40.1**	**33.3**

Figure 12. UV/Vis-NIR spectrum of fluorinated VO_2 films with the dashed lined representing the 4 mg VO_2/10 mL of methacrylic acid/ethyl acrylate solution, solid line representing the 6 mg/10 mL VO_2 sample, and the dotted line representing the 8 mg/10 mL VO_2 sample.

The fluorinated VO_2 produced some impressive modulation, which is depicted in figure 12. The drop in the NIR hit 41% for the 6 mg sample. Alone this data stands for having good dispersion throughout the film, but the maximum transmittance percentage is also an important factor. The transmittance for this 6 mg sample is at 40.4 %, as seen in figure 12, and this demonstrates that it is possible to have high drops in the NIR while also maintaining a good percentage in the maximum transmittance.

Film Application of Functionalized & Stöber Optimized Silica Coated Vanadium Dioxide

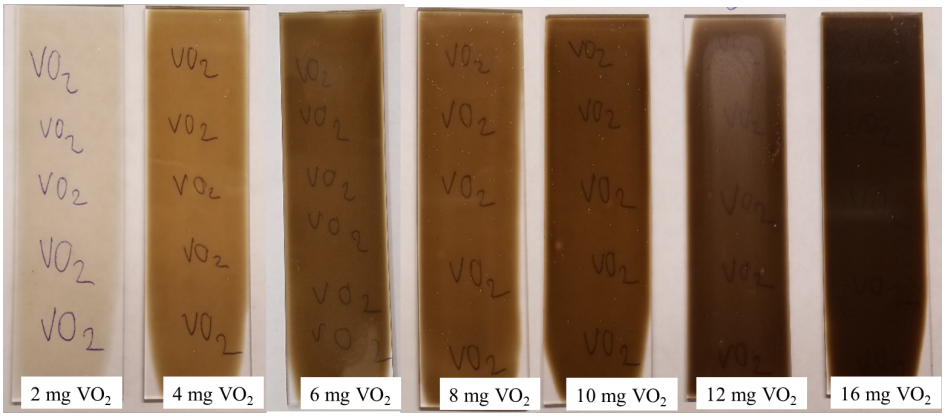


Figure 13. From left to right, films cast using 2 mL of solution from 10 mL stock containing a total of: 2, 4, 6, 8, 10, 12, 16 mg fluorinated VO_2@SiO_2 in 10 mL of methacrylic acid/ethyl acrylate solution. Each coated *via* casting knife.

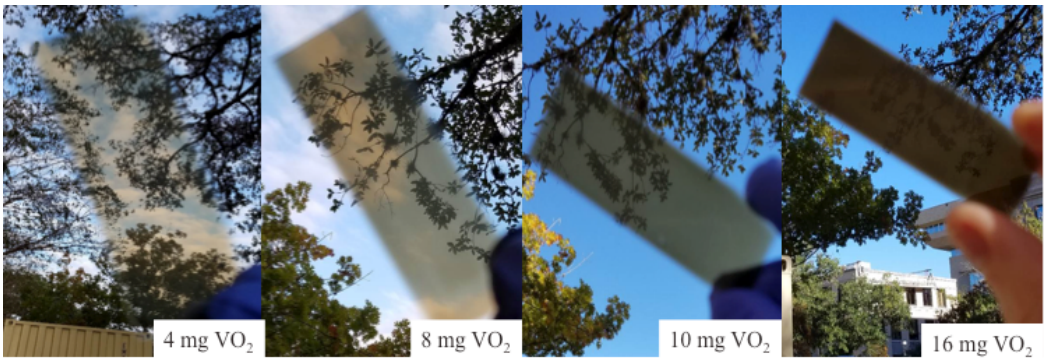
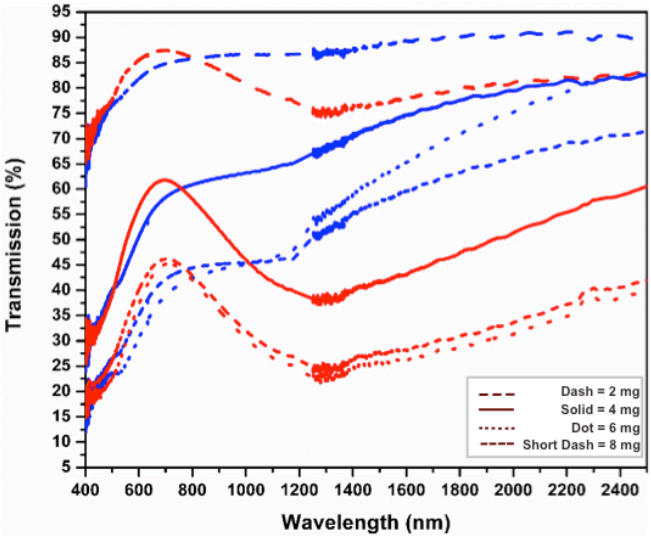


Figure 14. From left to right: images of 4, 8, 10, 16 mg of VO_2 in 10 mL of methacrylic acid/ethyl acrylate solution. Films were cast from fluorinated VO_2@SiO_2 solutions and coated *via* casting knife and exposed to natural light.

To determine the degree of success in reducing agglomeration by use of functionalized VO_2 and the optimized Stöber method, films were created from functionalized VO_2@SiO_2 nanoparticles. These nanoparticles were silica coated with the optimize parameters of the Stöber method. Casting of these films, as seen in figures 13 and 14, produced uniform films overall, as

dispersion of the VO_2 particles was increased with the use of the fluorinating surfactant. These films were created with only varying amounts of VO_2 to determine how much VO_2 is required to produce higher degrees of modulation while maintaining high visible light transmission.



	NIR drop (%)	Max Vis (%)
2 mg/10 mL	**12.0**	**87.5**
4 mg/10 mL	**31.7**	**61.8**
6 mg/10 mL	**44.5**	**45.2**
8 mg/10 mL	**33.0**	**46.2**

Figure 15. UV/Vis Spectrum of fluorinated VO_2@SiO_2 films with the dashed lines representing the 2 mg/10 mL VO_2 films, solid lines representing the 4 mg/10 mL VO_2 sample, and the dotted lines representing the 8 mg/10 mL VO_2 sample.

In figures 13 and 14, it is shown that, with an increase of the concentration of VO_2, the transmission in the visible spectra consequently drops as is apparent in the UV-VIS data in figure 15. From this data, it can also be concluded that with an increase of the concentration of VO_2 the percentage drop in the NIR also increases. A large drop in the transmission NIR provides data in

the dispersion of the nanoparticles across the films. If there is a very large drop in the NIR with an early onset of modulation and small concentration of VO_2, it can be surmised that these nanoparticles were well dispersed throughout the film. In the five samples produced from $VO_2@SiO_2$ the most successful films was the 6 mg/10 mL sample producing a drop of 44.5 % in the NIR which is the largest drop recorded for any of the samples. This sample also yielded a reasonable transmission in the visible spectra at 45.2 %. When comparing UV-Vis-NIR transmission spectra for both $VO_2@SiO_2$ and VO_2-F, it is apparent that the overall percentage for NIR drops in all the samples for the $VO_2@SiO_2$ are much lower than VO_2. This is due to the fact that VO_2 was not coated with the optimized Stöber method that was identified previously in this work.

CHAPTER IV

CONCLUSION

In conclusion it was found that the Stöber method at 50 μL TEOS and 400 μL NH_4OH with a reaction time of 20 min produced the most successful sample by yielding silica shells with a shell thickness range of 5-7 nm. Surface functionalization of VO_2/VO_2@SiO_2 also produced successful samples as the agglomeration of VO_2 nanoparticles was greatly reduced as seen by producing a drop of 44% in the NIR spectra while maintaining a high degree of visible transmission. Overall, the agglomeration of VO_2 nanoparticles was substantially reduced through the optimization of the Stöber method as well as surface functionalization of VO_2 nanoparticles. This research provides a step forward in the application of smart windows as it provides a mean of reducing overall agglomeration of VO_2 nanowires in film and providing better dispersion of VO_2 in solution from these results, films can be produced to provide better visible transmittance and well as appreciable drop in the NIR.

REFERENCES

1. US Department of Energy, Energy Efficiency Trends in Residential and Commercial Buildings, Washington DC **2008**.

2. Luisa Whittaker, Christopher J. Patridge, and Sarbajit Banerjee, *The Journal of Physical Chemistry Letters* **2011** *2* (7), 745-758.

3. Whittaker, L.; Velasquez, J. M.; Banerjee, S. *CrystEngComm* **2011,** 13, 5328.

4. G. A. Horrocks, S. Singh, M. F. Likely, G. Sambandamurthy and S. Banerjee, *ACS Appl. Mater. Interfaces*, **2014**, 6, 15726–15732.

5. Li, W., Ji, S., Qian, K. & Jin, P, *Ceram. Int.* **2015,** 41**,** 5049–5056

6. Zhu, J. *et al., ACS Appl. Mater. Interfaces* **2015,** 7, 27796–27803

7. Pelcher, K. E.; Crawley, M. R.; Banerjee, S. *Mater. Res. Express* **2014**, 1, 035014.